Diffusion-limited annihilation in inhomogeneous environments

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We study diffusion-limited (on-site) pair annihilation $A + A \to 0$ and (on-site) fusion $A + A \to A$ which we show to be equivalent for arbitrary *space-dependent* diffusion and reaction rates. For one-dimensional lattices with nearest neighbour hopping we find that in the limit of infinite reaction rate the time-dependent n-point density correlations for *many-particle* initial states are determined by the correlation functions of a dual diffusion-limited annihilation process with at most $2n$ particles initially. Furthermore, by reformulating general properties of annihilating random walks in one dimension in terms of fermionic anticommutation relations we derive an exact representation for these correlation functions in terms of conditional probabilities for a *single* particle performing a random walk with dual hopping rates. This allows for the exact and explicit calculation of a wide range of universal and non-universal types of behaviour for the decay of the density and density correlations.

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1 Introduction

In this paper we investigate a class of models describing diffusion-limited annihilation of identical particles. This is a process where particles of a single species diffuse (rather than move ballistically) and undergo an annihilation reaction when two particles meet. The outcome of such a reaction may be either a single particle, or both particles disappear. This process can describe both chemical reactions where the particles change their state into an inert reaction product which takes no part in the subsequent dynamics of the system, or physical reactions where the particles actually annihilate under the emission of radiation. On an abstract level, both kinds of reactions are identical. A known one-dimensional process with "physical" annihilation is e.g. laser-induced exciton dynamics on polymers [1]. Clearly, one is not interested in the equilibrium behaviour of such a model, since in the absence of continued particle production all particles eventually disappear. Instead one would like to understand non-equilibrium properties such as the time-dependence of the particle concentration for a given initial condition and the degree of universality obtained from specific choices of models.

Diffusion-limited pair annihilation of particles of a single species is a well-studied system (for a recent review see [1]), but there are still interesting open questions particularly in the presence of spatially inhomogeneous hopping and reaction rates which have so far not been addressed. In homogeneous, translationally invariant environments the particle density decays with a power law which depends on the dimensionality of the system. Both theoretically and experimentally one finds $\rho(t) \sim 1/\sqrt{Dt}$ in one dimension.

Interestingly, this result is at variance with the dimensionality-*in*dependent mean-field behaviour $\rho(t) \sim 1/(Dt)$ which is correct only in three (and higher) dimensions. The amplitude of this decay is universal in the sense that it depends neither on the initial density for random initial conditions nor on the reaction rate [2]. However, if particles are moving in an arbitrary, non-translationally invariant energy landscape it is not obvious how this will change the decay of the local or overall particle concentration. In our study which is a continuation of previous work [3] we first discuss universality of a general class of models, but then shall pay special attention to one-dimensional systems with nearest neighbour interaction. The physical motivation behind the study of one-dimensional system is not only their experimental relevance for polymer physics, but also their theoretical importance in the understanding of the role of fluctuations in low-dimensional systems. In both one- and two-dimensional systems diffusive mixing is inefficient and leads to the building up of large-scale correlations. Thus the classical mean-field rate equations for the study of these systems tend to fail and require a more sophisticated treatment.

To this end we investigate by exact methods a family of lattice models with space-dependent hopping and pair annihilation rates, as one would have e.g. in disordered systems or in the presence of a space-dependent external forces affecting the diffusive motion of the particles. These particles have no attractive or repulsive interaction between themselves, they hop with fixed rates d_{xy} from lattice site x to site y. When two particles meet on site x they both annihilate with a rate λ_x. We address two different problems: (1) The first is to identify other systems which are in the same universality class

in any dimension. In fact, our approach of using similarity transformations extends to systems defined on arbritrary lattices. This idea is not new for systems with exclusion dynamics [4] - [8]. Here we extend the application of similarity transformations to models without site-exclusion. This generalization is useful for a renormalization group treatment of the problem [9, 2, 10] as it yields exact relations for expectation values for one model in terms of expectation values for the related system without any further RG analysis for each of these different models. (2) Since the RG treatment shows that the fixed point of the homogeneous system with nearest neighbour hopping is the limit of infinite reaction rate, and since mean-field is particularly poor in one dimension, the second problem we address is a more detailed investigation of the one-dimensional case in the limit of infinite reaction rate but with (arbitrary) space-dependent nearest neighbour hopping rates. Here we use not only similarity transformations but also free fermion techniques which, as shown below, are a convenient framework to formulate general properties of annihilating random walks in one dimension. From our treatment we find that the time-dependent density correlations for an arbitrary *many-particle* initial state have an exact representation in terms of conditional probabilities for a *single* particle performing a random walk with dual hopping rates. In the case of constant hopping rates the predictions of this model are in excellent agreement with experimental data on exciton dynamics on very long ordered polymer chains. Thus we expect that our model gives an equally good description of the behaviour of inhomogeneous systems.

The paper is organized as follows. In Sec. 2 we briefly review the description of reaction-diffusion processes in terms of a master equation which

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is written in a quantum Hamiltonian formalism. In Sec. 3 equivalences between models without site exclusion are studied. This is extended in Sec. 4 to the limit of infinite reaction rate and nearest neighbour hopping and the main results of the paper are derived. In Sec. 5 some specific results for random initial conditions are derived and in Sec. 6 the main results are summarized and discussed.

2 Quantum Hamiltonian formalism for stochastic reaction-diffusion systems

The reaction-diffusion processes considered in this work are systems of *classical* interacting particles which hop stochastically on a lattice and undergo some reaction when they meet on the same lattice site. For definiteness we shall consider only systems of one species of particles even though most of what is discussed in this and the following Section can be generalized to systems of many species. In symbolic presentation particles are denoted by A, a vacant site by $\emptyset$. The expression kA denotes the presence of k particles are in the same site.

We define the process in terms of a master equation for the probability $P(\eta; t)$ of finding, at time t, any configuration η of particles on a lattice S of $\mathcal{L}$ sites. Here $\eta = \{\eta(1), \eta(2), \ldots, \eta(\mathcal{L})\}$ where $\eta(x)$ are the integer-valued particle occupation numbers at site x. The lattice is at this stage arbitrary. Later, when discussing one-dimensional systems we consider only linear chains with $\mathcal{L} = L$ sites and periodic boundary conditions. For clarity we shall use in this case site labels k, l, m instead of x, y, z.

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A general master equation reads

$$\frac{d}{dt}P(\eta';t) = \sum_{\eta \neq \eta'} \{w(\eta',\eta)P(\eta,t) - w(\eta,\eta')P(\eta';t)\} \tag{1}$$

The positive contribution to the (infinitesimal) change in probability is the sum of probabilities that the system has been in a state η times the rate $w(\eta',\eta)$ of flipping to η'. The rates satisfy $0 \leq w(\eta',\eta) < \infty$ and define the exponentially distributed life time $\tau^{-1}(\eta') \equiv \sum_{\eta \neq \eta'} w(\eta,\eta')$ of a state η'. This is the total rate for the state η' to flip into any other configuration and hence represents the loss in probability for the state η' in Eq. (1). We shall now express the time evolution given by the master equation in terms of a quantum Hamiltonian H. This is discussed in detail in [13] and also in earlier work [14, 15, 16] and we shall repeat only the essential elements of the mapping. The advantage of this approach is that there are standard methods of dealing with the resulting time evolution operator H. The applicability of these techniques, in the case at hand primarily similarity transformations and the renormalization group technique for systems without site exclusion and free fermion techniques for models with site exclusion, does not arise naturally if the master equation is written down in the standard form (1).

2.1 Definitions

The idea is to represent each of the possible particle configurations η in the set $X = \mathbb{N}^{\mathcal{L}}$ by a vector $|\eta\rangle$ which together with the transposed vectors $\langle\eta|$ form an *orthonormal* basis of a vector space $X = (\mathbb{C}^{\infty})^{\otimes L}$. The basis is chosen such that for a single site the state $|n\rangle$ with $\eta(x) = n$ particles is represented by the unit column vector with a 1 at the nth position and

zero elsewhere. Then the state of the lattice as a whole is represented by the tensor product $|\eta\rangle = |\eta(1)\rangle \otimes \ldots \otimes |\eta(\mathcal{L})\rangle$. Now one can conveniently represent the probability distribution by a state vector

$$|P(t)\rangle = \sum_{\eta \in X} P(\eta; t)|\eta\rangle. \tag{2}$$

Using $P(\eta; t) = \langle \eta | P(t) \rangle$ one writes the master equation (1) in the form

$$\frac{d}{dt}P(\eta; t) = -\langle \eta |H| P(t) \rangle \tag{3}$$

where the off-diagonal matrix elements of H are the (negative) transition rates and the diagonal entries are the life times of the states.

Therefore the time evolution of this probability vector is given in terms of a linear 'Hamilton' operator H acting on X

$$\frac{d}{dt}|P(t)\rangle = -H|P(t)\rangle. \tag{4}$$

A state at time $t = t_0 + \tau$ is given in terms of an initial state at time t_0 by

$$|P(t_0 + \tau)\rangle = \mathrm{e}^{-H\tau}|P(t_0)\rangle. \tag{5}$$

Note that $\langle s | P(t) \rangle = \sum_{\eta \in X} P(\eta; t) = 1 \ \forall \, t$ where

$$\langle s| = \sum_{\eta \in X}\langle \eta| \tag{6}$$

This relation expresses conservation of probability and implies

$$\langle s|H = 0 \tag{7}$$

for any stochastic process. We shall call a matrix which satisfies (7) and $H_{\eta,\eta'} \leq 0$ for all off-diagonal elements a *stochastic Hamiltonian*.

This definition is manifestly basis dependent. If a stochastic Hamiltonian H is related to some other Hamiltonian $\tilde{H}$ by a similarity transformation,

$$H = B\tilde{H}B^{-1} \tag{8}$$

we shall call the systems *equivalent*, irrespective of whether $\tilde{H}$ is stochastic or not. If $\tilde{H}$ is stochastic, then the two processes are called equivalent. An equally useful relation is

$$H = B\tilde{H}^T B^{-1} \tag{9}$$

relating a stochastic process to the transpose of a matrix $\tilde{H}$. If both H and $\tilde{H}$ are stochastic, we shall say that these two processes are *enantiodromic* with respect to each other. Any family of transformations B generates a family of related processes (equivalent or enantiodromic). Any one member of this family is called a *representative*.

Expectation values $\langle Q(t) \rangle = \langle s | Q | P(t) \rangle$ are calculated as matrix elements of suitably chosen diagonal operators Q. A complete set of observables are the occupation numbers $\eta(x)$. Defining projection *operators* on states with n particle on site x of the lattice as

$$Q_x(n) = | n \rangle_x \langle n |_x \tag{10}$$

one finds that the density $\rho_x(t)$ of particles at site x is given by the expectation value $\langle n_x \rangle$ of the operator $n_x = \sum_{n=0}^{\infty} n Q_x(n)$. This is the diagonal matrix n acting non-trivially only on site x with matrix elements $(n)_{kl} = k\delta_{k,l}$. Density orrelation functions $\langle n_{x_1} \cdots n_{x_j} \rangle$ are computed analogously.

For later convenience we also introduce the operators $a_x^{\pm}$. The single-site

matrix a^+ has elements $(a^+)_{m,n} = \delta_{m,n+1}$. Hence

$$a^+ \,|\, n \,\rangle = |\, n+1 \,\rangle \,, \ \langle\, n \,|a^+ = \langle\, n-1 \,|. \tag{11}$$

creates a particle with unit rate when acting to the right. The single-site matrix a^- has elements $(a_x^-)_{m,n} = n\delta_{m,n-1}$. Thus

$$a^- \,|\, n \,\rangle = n|\, n-1 \,\rangle \,, \ \langle\, n \,|a^- = (n+1)\langle\, n+1 \,|. \tag{12}$$

annihilates a particle, but with a rate proportional to the occupation number prior to the annihilation. This corresponds to annihilating any one of the existing identical particles with unit rate. It is understood in these equations that $a^- \,|\, 0 \,\rangle = \langle\, 0 \,|a^+ = 0$. Note that the matrices $a^\pm$ satisfy a harmonic oscillator algebra $a^- a^+ - a^+ a^- = 1$. The product $n = a^+ a^-$ is the number operator. Matrices acting on different sites commute.

The state $\langle\, s \,|$ is the coherent state $\langle\, s \,| = \langle\, 0 \,| \exp{(A^-)}$ where $A^\pm = \sum_x a_x^\pm$ and $\langle\, 0 \,| \equiv (\langle\, 0 \,|)^{\otimes \mathcal{L}}$ is the row vector representing the completely empty lattice. Using the harmonic oscillator algebra and the factorization of $\exp{(A^-)}$ one finds the following relations

$$\langle\, s \,|a_x^+ = \langle\, s \,| \,, \ \langle\, s \,|a_x^- = \langle\, s \,|n_x \tag{13}$$

which are useful for the construction of the Hamiltonian H and for the derivation of the equations of motion for correlation functions.

In the infinite reaction limit discussed below, the system we investigate reduces to a two-state model where each lattice site is either empty or occupied and the state space reduces to $X = (\mathbb{C}^2)^{\otimes \mathcal{L}}$. For this situation is more convenient to use Pauli matrices σ_k^α acting on site k for the description of

the elementary events of the stochastic time evolution. A complete set of observables are now the occupation numbers $n_k = 0, 1$. Projectors on states with a particle on site k of the chain are then defined by the diagonal matrix

$$n_k = \frac{1}{2}\left(1 - \sigma_k^z\right). \tag{14}$$

One may equally well use spin language. In this interpretation n_k projects on a spin down at site k and $v_k \equiv 1 - n_k$ projects on vacancies or spin up respectively.

Changes in the occupation numbers are effected by $s_k^{\pm} = (\sigma_k^x \pm i\sigma_k^y)/2$. In our convention s_k^- creates a particle at site k when acting to the right, while s_k^+ annihilates a particle at site k.[1] Note that

$$\langle\, s\,|s_k^+ = \langle\, s\,|n_k \quad \text{and} \quad \langle\, s\,|s_k^- = \langle\, s\,|(1 - n_k). \tag{15}$$

Introducing the ladder operators $S^{\pm} = \sum_{k=1}^{L} s_k^{\pm}$ one may write

$$\langle\, s\,| = \langle\, 0\,|\, \mathrm{e}^{S^+}. \tag{16}$$

Using the commutation relations for the Pauli matrices then yields (15).

Some particular initial states and initial distributions used below: An initial state with N particles place on sites $x_1, \ldots, x_N$ is denoted by $|\, x_1, \ldots, x_N \,\rangle$. An uncorrelated initial state with a site-independent Poisson distribution is denoted by $|\,\rho\,\rangle$ where ρ stands collectively for all average site-densities ρ_x. The vector representing this inhomogeneous product measure is the factorized state $|\,\rho\,\rangle = \prod_x |\, P_0(x)\,\rangle$ where $|\, P_0(x)\,\rangle = \exp\left[\rho_x(a_x^+ - 1)\right]|\, 0\,\rangle$. For two-state models the same notation is used for an uncorrelated initial state with

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[1]This somewhat counterintuitive notation results from long standing convention which we do not wish to change.

bimodal distribution. In this case, the probability of finding site x occupied is ρ_x and the probability of finding it vacant is $1 - \rho_x$. The completely empty lattice is always represented by the vector $|\,0\,\rangle$.

2.2 Construction of the quantum Hamiltonian

Now we are in a position to derive H. The process we consider as a representative is defined by following elementary rules:

- Particles move on a lattice from sites $x \to y$ with a fixed rate $p(x, y)$ which is not necessarily symmetric.

- Any two particles on a site can annihilate with rate $\tilde{\lambda}(x)$.

The idea behind these rules is the description of particles which have no physical interaction (repulsive or attractive), but only a chemical interaction which allows the formation of an inert product from two single particles which then has no influence on the subsequent dynamics. In this model no assumptions are made about the physical or chemical origin of the space dependence of these rates.

The precise nature of the dynamics is defined by a master equation (1). With matrices defined above the stochastic quantum Hamiltonian for the process has the form $H^I = H_D^I + H_R^I$ where H_D^I describes hopping $H_R^I = \sum_x h_x^I$ describes annihilation. It is given by

$$H^I = -\sum_{x \neq y \in S} p(x, y)(a_x^- a_y^+ - n_x) - \sum_{x \in S} \tilde{\lambda}(x) \left((a_x^-)^2 - n_x(n_x - 1) \right). \quad (17)$$

The first sum runs over all pairs (x, y) of sites of the lattice S and describes hopping of non-interacting particles from x to y whereas the second sum

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runs over all sites of the lattice and gives the annihilation events. According to the general rules the off-diagonal part represents the possible moves the system can perform in an infinitesimal time step. The diagonal part ensures that probability is conserved. Using (13) and the harmonic oscillator algebra it is easy to check that (7) holds for each elementary process and hence for H.

Consider now the infinite annihilation limit $\tilde{\lambda}(x) = \lambda(x)/\lambda_0$ with $\lambda_0 \to 0$. In practical terms this means that the time scale λ_0 on which the annihilation takes place is much shorter than the time scales $p(x, y)$ set by the hopping events. In this limit two things happen: Firstly, in the initial state any site occupancy by an even number of particles is immediately reduced to a vacancy and any site with an odd number of particles is left with just a single particle. Secondly, if by a hopping event a double occupancy is created, this results immediately in a pair of empty sites. Thus an attempted hopping event of the form $A_x A_y \to \emptyset_x 2A_y$ with rate $p(x, y)$ is equivalent to the pair annihilation process $A_x A_y \to \emptyset_x \emptyset_y$ with rate $p(x, y)$. In short, the system becomes equivalent to an exclusion process with particle hopping and pair annihilation with annihilation rates that are equal to the sum of the hopping rates $p(x, y) + p(y, x)$. The Hamiltonian for this process reads in terms of Pauli matrices

$$H^{II} = -\sum_{x \neq y} p(x, y)(s_x^+ s_y^- + s_x^+ s_y^+ - n_x). \tag{18}$$

This can be derived in a more formal way using the infinite rate formalism of [13]. The two systems I and II defined by (17), (18) are subject of this paper. The infinite rate model (18) will be studied in some detail in one dimension

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with nearest neighbour events ($p(x,y) = 0$ for $y \neq x \pm 1$).

Since the process conserves particle number modulo 2, it splits into two distinct subsectors corresponding to even and odd numbers of particles. For the two state process (18) the operator

$$Q = \prod_{k=1}^{L} \sigma_k^z = (-1)^N \tag{19}$$

has eigenvalue ± 1 in the even (odd) sector respectively. Hence $P^{\pm} = (1 \pm Q)/2$ projects on these sectors. Corresponding to this separation of the dynamics it is convenient to use

$$\langle\, s\,|^{even,odd} = \langle\, s\,|\, P^{\pm} \tag{20}$$

instead of $\langle\, s\,|$ for the calculation of expectation values.

3   Similarity transformations for DLPA

We want to consider equivalences between model I and other systems of particles hopping on a lattice and which, independently of the hopping process, undergo some reaction when they meet on the same lattice site. I.e. we are looking for a stochastic process of the form $\hat{H} = \hat{H}_D + \hat{H}_R$ such that $\hat{H} = \mathcal{B} H \mathcal{B}^{-1}$ and where $\hat{H}_D$ describes hopping on non-interacting particles and where $\hat{H}_R = \sum_x \hat{h}_x$ describes some on-site chemical interaction. Attempting to identify all possible equivalent systems appears to be a hopeless enterprise which is the reason why we restrict ourselves to equivalent processes with only on-site interaction. Therefore we assume $\mathcal{B}$ to factorize, $\mathcal{B} = B_1 \otimes \ldots \otimes B_{\mathcal{L}}$. This has a consequence for the choice of B_x itself:

The transformed hopping Hamiltonian $\hat{H}_D$ should not contain two-site operators other than the hopping matrices $a_x^+ a_y^-$ as such objects not describe non-interacting particles or strictly local interactions as demanded. This requirement is met by a matrix $B_x = \exp\left(\alpha_x a_x^- + \beta_x a_x^+ + \gamma_x n_x + \delta_x\right)$ with arbitrary parameters $\alpha_x, \beta_x, \gamma_x, \delta_x$. Since $\langle s |$ has to remain invariant under the transformation, one has to choose $\gamma_x = -\alpha_x$ and $\delta_x = -\beta_x$. This leaves a family of transformations with $2\mathcal{L}$ free parameters.

Using the harmonic oscillator algebra one shows that

$$Ba^- B^{-1} = e^\alpha a^- + \frac{\beta}{\alpha}(1 - e^\alpha) \tag{21}$$

$$Ba^+ B^{-1} = e^{-\alpha} a^+ + 1 - e^{-\alpha} \tag{22}$$

which are necessary for the calculation of $\hat{H}$. Applying the transformation to H_R^I shows that positivity and reality of the transformed rates constrains the transformation parameters to be in the domain $-\ln 2 \leq \alpha_x \leq 0$, $\beta_x = 0$. Any transformation with $\beta_x \neq 0$ leads to events with negative rate. Even though this can be compensated by inclusion of particle creation events in the original Hamiltonian, we do not consider this possibility in the present work.[2] If $\beta = 0$ the hopping part H_D^I is invariant under the transformation if one chooses the transformation parameters $\alpha_x = \alpha$ space-independent. Thus a transformation meeting all the requirements discussed above gives rise to the one-parameter family of processes

$$\hat{H}^I = -\sum_{x \neq y \in S} p(x, y)(a_x^- a_y^+ - n_x)$$

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[2]We just note for illustration that inclusion of single particle annihilation $A \to \emptyset$ and pair creation $\emptyset \to 2A$ with suitably chosen rates is equivalent to a process with pair annihilation, branching $A \to 2A$ and creation $\emptyset \to A$ under a transformation with $\beta \neq 0$.

$$-\sum_{x \in S} \tilde{\lambda}(x) \left[(1 - b + ba_x^+)(a_x^-)^2 - n_x(n_x - 1) \right]. \tag{23}$$

where particle either annihilate $2A \to 0$ with rate $(1 - b)\lambda_x$ or undergo a fusion reaction $2A \to A$ with rate $b\lambda_x$ where $b = 2(1 - \exp(\alpha))$. This shows that pair annihilation and fusion are in the same universality class irrespective of the lattice on which the system is defined and also irrespective of the physical environment specifying the rates $p(x, y)$ and $\lambda(x)$. The choice of lattice is completely arbitrary. The equivalence of the two processes was first discovered by Krebs et al. [5] for a model with site-exclusion and homogeneous nearest neighbour hopping in one dimension. Universality for finite reaction rate in any dimension was shown by Peliti [9] using the RG approach.

Since the mapping defined by the transformation $\mathcal{B}$ is exact it is worthwhile to investigate some of the consequences for expectation values for the two processes. First we note that both $\langle s |$ and $\mathcal{B}$ factorize and therefore $\langle s | B = \langle s |$. To proceed, we consider as initial state uncorrelated random initial conditions with site-dependent density ρ_x, i.e. we assume that at time zero particles have been distributed randomly and independently at each site with a Poisson distribution $P_x(n) = \exp(-\rho_x)\rho_x^n/n!$. This can be achieved by filling an originally empty lattice by the process $H = -\sum_x \rho_x/\tau(a_x^+ - 1)$ up to a time $t = \tau$. Then the creation is switched of and annihilation and fusion take place. For the pure annihilation process the concentration $\rho_y(t)$ of particles at site y is given by $\rho_y(t) = \langle s | n_y \exp(-H^I t) | \rho \rangle$. In order to relate the density

$$\hat{\rho}_y(t) = \langle s | n_y B^{-1} e^{-H^I t} B | \rho \rangle \tag{24}$$

for the mixed process to $\rho_y(t)$ we have to study the effect of the transforma-

tion on both $|\,\rho\,\rangle$ and n_y. A short calculation shows that $B|\,P_0(x)\,\rangle$ remains a Poisson distribution, but with density $\hat{\rho}_x = \rho_x \exp(-\alpha)$. On the other hand, (13) together with (21) yields $\langle\,s\,|Bn_y B^{-1} = \langle\,s\,|a_y^- B^{-1} = \exp(\alpha)\langle\,s\,|n_y$. This gives

$$\hat{\rho}_y(t) = e^\alpha \rho_y(t) \tag{25}$$

where the initial densities for the mixed process are related to the initial density of the pure annihilation process by the relation $\hat{\rho}_x = \rho_x \exp(-\alpha)$. For a k-point correlation function $F(x_1, \ldots, x_k; t) = \langle\, n_{x_1}(t) \ldots n_{x_k}(t)\,\rangle$ where all x_i are pairwise different, (25) generalizes to

$$\hat{F}(x_1, \ldots, x_k; t) = e^{k\alpha} F(x_1, \ldots, x_k; t). \tag{26}$$

If two or more coordinates are equal, one has to use (21) and (22). For the two-point function $F_2(y; t) = \langle\, n_y^2(t)\,\rangle$ this yields

$$\hat{F}_2(y; t) = e^{2\alpha} F_2(y; t) - e^\alpha (1 - e^\alpha)\rho_y(t). \tag{27}$$

It is interesting to consider the ratio $\Delta(t) = \langle\, N^2(t)\,\rangle - \langle\, N(t)\,\rangle^2 / \langle\, N(t)\,\rangle$ of the particle number fluctuations to the particle number $\langle\, N\,\rangle = \sum \langle\, n_x\,\rangle$ at time t. For the mixed process one obtains the exact relation $\hat{\Delta}(t) = \exp(\alpha)(\Delta(t) - 1) + 1$. This relation can be used to measure the branching ratio of an experimental system, if one can measure both the average particle number and its fluctuations and if Δ for the pure annihilation process can be calculated analytically for the respective physical environment. In the simplest case of infinite pure annihilation and homogeneous nearest neighbour hopping in one dimension this quantity can be calculated exactly [13] and

is for sufficiently large times independent of time and of the initial density, $\Delta(t) \to 2 - \sqrt{2}$.

4   Infinite reaction limit

The transformation of the last section is independent of $\lambda(x)$. Therefore all the results translate with little modification into the dynamics of the exclusion process H^{II} defined in (18) which describes the dynamics with infinite reaction rate. One just has to replace $a^- \to s^+$ in the transformation B, the results concerning the relations between correlation functions remain unchanged.

However, this simple observation is not all there is to say about this limit. It is known that in one dimension with nearest neighbour hopping DLPA is related to zero-temperature Glauber dynamics by a domain-wall duality transformation [17]. This transformation was shown recently to be an invertible similarity transformation [18]. On the other hand, it was noted that zero-temperature Glauber dynamics can be brought by another similarity transformation into a form which is the *transpose* of the Hamiltonian for DLPA [7]. From this we conclude that there must be a matrix $\mathcal{D}$ such that

$$H^{II} = \mathcal{D}^{-1}(H^{II})^T \mathcal{D}, \tag{28}$$

i.e. DLPA in one dimension with nearest neighbour hopping is self-enantiodromic in addition to being equivalent to the mixed pair-annihilation/fusion process.[3]

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[3] Strictly speaking, this applies only to the sector with an even number of particles. For an odd number of particles the situation is slightly more complicated.

From now on we consider only the one-dimensional process on a ring with L sites and with arbitrary nearest neighbour hopping rates $l_k = p(k, k-1)$ and $r_k = p(k, k+1)$. In order to avoid unnecessary technical complications with boundary terms, we consider only the sector with an even number of particles. Combining the results of Refs. [18, 7] yields

$$\mathcal{D} = \gamma_1 \gamma_2 \dots \gamma_{2L-1} \tag{29}$$

where

$$\gamma_{2k-1} = \frac{1}{2}\left[(1+i)\sigma_k^z - (1-i)\right] \tag{30}$$

$$\gamma_{2k} = \frac{1}{2}\left[(1+i)\sigma_k^x \sigma_{k+1}^x - (1-i)\right]. \tag{31}$$

To prove the enantiodromy relation (28) one notes that $\mathcal{D}$ is unitary and transforms Pauli matrices as follows:

$$\mathcal{D}^{-1}\sigma_k^x \sigma_{k+1}^x \mathcal{D} = \begin{cases} \sigma_k^z & k \neq L \\ Q\sigma_L^z & k = L \end{cases} \tag{32}$$

$$\mathcal{D}^{-1}\sigma_{k+1}^z \mathcal{D} = \begin{cases} \sigma_k^x \sigma_{k+1}^x & k \neq L \\ Q\sigma_L^x \sigma_1^1 & k = L \end{cases} \tag{33}$$

where $Q = \prod_{k=1}^{L} \sigma_k^z = (-1)^N$. For the even particle sector where $Q = 1$ the relation (28) follows for constant rates $l_k = r_k = D$.

In order to apply enantiodromy to inhomogeneous systems we first rewrite the Hamiltonian (18) adapted to the present case. For hopping rates as defined above the Hamiltonian reads

$$H = -\sum_{k=1}^{L}(r_k h_k^+ + l_k h_k^-) \tag{34}$$

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with the hopping-annihilation matrix $h_k^{\pm} = s_k^+ s_{k\pm1}^- + s_k^+ s_{k\pm1}^+ - n_k$. Applying the transformation yields the process $\hat{H} = \mathcal{D}^{-1} H^T \mathcal{D}$ given by

$$\hat{H} = -\sum_{k=1}^{L}(r_k h_k^- + l_k h_{k-1}^+).\tag{35}$$

The enantiodromic process is of the same form (34) as the original process, but with dual hopping rates

$$\hat{\ell}_k = r_k, \quad \hat{r}_k = l_{k+1}.\tag{36}$$

We shall refer to the environment defined by the dual rates as to the dual environment. The sector with an odd number of particles can be transformed in a similar way using $\mathcal{D}' = \mathcal{D}\sigma_L^x$. Some care needs to be taken in the treatment of the boundary term.

In order to make practical use of the enantiodromy we note

$$\langle s|^{even} n_{k_1} \ldots n_{k_m} e^{-Ht}| P_0 \rangle = \frac{1}{2^m}\langle P_0 |\mathcal{D} e^{-\hat{H}t}(1 - \sigma_{k_1-1}^x \sigma_{k_1}^x) \ldots (1 - \sigma_{k_m-1}^x \sigma_{k_m}^x)\mathcal{D}^{-1}| s \rangle^{even}.\tag{37}$$

This may be written in the form

$$\langle s|^{even} n_{k_1} \ldots n_{k_m} e^{-Ht}| P_0 \rangle = \langle s|Q e^{-\hat{H}t}| P_0' \rangle\tag{38}$$

where Q is determined by the original initial condition and the initial state $|P_0'\rangle$ is determined by the set of sites $\{k_1, \ldots, k_m\}$. The importance of this result is seen in the transformation law $\mathcal{D}^{-1}|s\rangle^{even} = -i(i-1)^{L-1}|0\rangle$. Hence $|P_0'\rangle$ is a linear combination of initial states of at most $2m$ particles. Since $\hat{H}$ does not have any particle creation terms the time-dependence of the m-point correlation function with an arbitrary many-particle initial state is

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completely determined by the dynamics of the system with not more than $2m$ particles. In particular, the density at site k is given by the dynamics of the dual system with just two particles placed initially at neighbouring sites $k - 1, k$.

It remains to consider the dynamics of Q. Without specifying the original initial distribution $|P_0\rangle$ and using (15) we can always write Q as a linear combination of products with an even number of particle annihilation operators $s_{l_1}^+ \ldots s_{l_{2p}}^+$ where $2p \leq 2m$ since $\hat{H}$ does not create particles. Now one can follow standard procedure and perform a Jordan-Wigner transformation [19, 20] by introducing $Q_k = \prod_{i=1}^{k} \sigma_i^z$ and the fermionic annihilation and creation operators

$$c_k^\dagger = s_k^- Q_{k-1} , \quad c_k = Q_{k-1} s_k^+ \tag{39}$$

satisfying the anticommutation relations $\{c_k, c_l\} = \{c_k^\dagger, c_l^\dagger\} = 0$ and $\{c_k^\dagger, c_l\} = \delta_{k,l}$. In terms of these operators Q can be written as a linear combination of products with an even number of fermionic particle annihilation operators $c_{l_1} \ldots c_{l_{2p}}$ and the initial state is of the form $c_{k_1}^\dagger \ldots c_{k_{2m}}^\dagger |0\rangle$. The Hamiltonian $\hat{H}$ is bilinear in $c_k^\dagger$, c_k and leads as shown in [20] to a linear time-evolution equation for $c_k(t) = \exp(\hat{H}t) c_k \exp(-\hat{H}t)$. The solution of the differential-difference equation obtained by taking the time-derivative of $c_k(t)$ is a single-particle problem, viz. the solution of the initial value problem of a single random walker in the hopping environment defined by $\hat{H}$, i.e.

$$c_k(t) = \sum_l \hat{P}(k; t|l, 0) c_l \tag{40}$$

where $\hat{P}(k; t|l, 0) = \langle k | \exp(-\hat{H}t) | l \rangle$ is the conditional probability for the single-particle problem. This reduces the calculation of the expectation value

of Q to the calculation of correlators of the form $\langle s \, | c_{l_1} \ldots c_{l_{2p}} c^\dagger_{k_1} \ldots c^\dagger_{k_{2m}} | 0 \rangle$ at time $t = 0$ which are given by the anticommutation relations and $c_l | 0 \rangle = 0$.

The appearance of free fermions in this problem of stochastic dynamics of classical interacting particles may seem surprising. However, to calculate the two-particle matrix transition probability $\langle m, n \, | e^{-\hat{H}t} | \, k, l \rangle$ one can either use the free fermion description, or, in a less technical way, remind oneselves of the meaning of an annihilating random walk and the description of random walks in terms of a sum over the canonical path space. In discrete space and time the transition probability (or conditional probability) for a single particle $\hat{P}(m; t | k, 0)$ is the sum over all paths leading from k to m, each weighted with its proper statistical weight given by the hopping rates and the particular form of the trajectory. If two non-interacting particles, one starting at site k and the other at site l, move, then the transition probability that the particle which started at site $k < l$ reaches site $m < n$ and the particles which started at site l reaches site n at time t is still the sum over all possible trajectories which connect k with m and l with n, where each single trajectory has the same weight as in the single particle case. Hence, for non-interacting particles, $\hat{P}(m, n; t | k, l; 0) = \hat{P}(m; t | k; 0) \hat{P}(n; t | l; 0)$. This sum includes the contribution of paths which cross each other. In an annihilating random walk of otherwise non-interacting particles the contribution of all crossing paths have to be subtracted. Since we are on a infinite, one-dimensional lattice and both particles are identical this contribution is just the one given by all paths which start at site k and end at site n (instead of m) and which start

at site l and end at site m (instead of n). Therefore

$$\hat{P}(m,n;t|k,l;0) = \hat{P}(m;t|k;0)\hat{P}(n;t|l;0) - \hat{P}(n;t|k;0)\hat{P}(m;t|l;0) \quad (41)$$

which is indeed what one obtains using the anticommutation relations in the free fermion approach. The same subtraction scheme generalizes to higher order conditional probabilities and is again conveniently captured in the free fermion anti-commutation relations.

The contents of this section is the main result of the paper. In the following section we consider some of its consequences. Further relations can be obtained in a straightforward manner for multi-time correlation functions.[4] The fact that $\hat{H}$ does not contain particle creation terms ensures that also the calculation m-point correlators for different times is reduced to the solution of the $2m$-particle problem. The reduction of an equal-time m-point correlator to a $2m$-particle problem for the one-dimensional model with homogeneous hopping rates was first observed in [21] using a mapping to a polymerization process. The new results presented here are the systematic and explicit way of expressing this reduction, its generalization to multi-time correlators and to non-translationally invariant systems and the final reduction to a single-particle problem in the dual environment.

5 Density decay

The result of the previous section is completely general as far as the hopping rates, observables and initial states are concerned. To be more spe-

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[4]In fact, all the results obtained here for equal-time correlations functions could have been phrased in more conventional language using the notion of duality as often done in the study of interacting particle systems.

cific we consider now as initial distribution an uncorrelated random initial state with density $1/2$ in the sector of even particle number. This distribution is represented by the vector $|1/2\rangle = 1/2^{L-1}|s\rangle^{even}$. We study the decay of the density in a so far unspecified, but fixed environment. One has $\langle 1/2|\mathcal{D} = i(-1-i/2)^{L-1}\langle 0|$ and thus

$$\rho_k(t) = \frac{1}{2}\langle 2|e^{-\hat{H}t}|k-1,k\rangle \tag{42}$$

where $\langle 2| = \sum_{n>m}\langle m,n|$ is the sum over all states with two particles. Hence *the density at site k at time t for a random initial distribution with density $1/2$ is equal to one half of the survival probability of finding two particles anywhere in the dual environment, where initially two particles have been placed at sites $k-1,k$.* The product form (41) of the two-particle conditional probability allows us to write

$$\rho_k(t) = \frac{1}{2}\sum_m \hat{P}_{m,k}\left[\hat{P}_{m,k} + \hat{P}_{m,k-1}\right]$$
$$- \sum_m \sum_{n=0}^{\infty} \hat{P}_{m,k}\left[\hat{P}_{m-n,k} - \hat{P}_{m-n-1,k-1}\right] \tag{43}$$

with $\hat{P}_{m,k} \equiv \hat{P}(m;t|k;0)$ as a short hand for the conditional probability.

The expression (43) contains a double sum. This can be reduced to a single sum by considering the time derivative for the density for which one gets

$$\frac{d}{dt}\rho_k(t) = -\frac{1}{2}\sum_m(\hat{r}_{m-1} + \hat{\ell}_m)\langle m-1,m|e^{-\hat{H}t}|k-1,k\rangle. \tag{44}$$

The density at the boundary of a semi-infinite system, i.e. an infinite system with vanishing boundary hopping rates $r_0 = \ell_1 = 0$ has an even

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simpler expression,

$$\rho_1(t) = \frac{1}{2} \sum_{n=1}^{\infty} \hat{P}(n; t | 1, 0).$$ (45)

In the dual system a particle which has moved to site 0 cannot escape from there (except by annihilation with a second particle hopping from site 1 to site 0). Thus the boundary density at time t for a random initial distribution with density $1/2$ is equal to one half of the survival probability of a single particle anywhere in the dual environment which has an absorbing boundary site 0 and where initially the particle has been placed at sites 1.

Eqs. (42) - (45) are exact and valid for any fixed environment. For further analysis we make two assumptions on the behaviour of the random walker. First consider site-symmetric processes with $r_k = \ell_k \equiv s_k$. In this case, the dual process is bond symmetric, $\hat{r}_k = \hat{\ell}_{k+1}$, and therefore $\hat{P}_{m,k} = \hat{P}_{k,m}$. For environments such that $\lim_{t \to \infty} \sum_n \left[\hat{P}_{m-n,k} - \hat{P}_{m-n-1,k-1} \right] / \hat{P}_{m-n,k} \to 0$ the second term in (43) becomes small compared to the first for large times. This expresses the density at site k

$$\rho_k(t) = \frac{1}{2} \left(\hat{P}(k; 2t | k; 0) + \hat{P}(k; 2t | k-1; 0) \right).$$ (46)

in terms of return probabilities of a random walker. In the presence of an average drift with drift velocity v such that $\hat{P}_{m,k} = \hat{P}_{2vt+k,m}$ the analogue of (46) reads $\rho_k(t) = (\hat{P}(k+2vt; 2t | k; 0) + \hat{P}(k+2vt; 2t | k-1; 0))/2$. Here v may be itself be explicitly time-dependent. If furthermore to leading order in time $\hat{P}(k+2vt; 2t | k; 0) = \hat{P}(k+2vt; 2t | k-1; 0)$, then one gets the simple result

$$\rho_k(t) = \hat{P}(k+2vt; 2t | k; 0).$$ (47)

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The time-dependence of the return probability depends on the environment.

6   Conclusions

The main results of this paper are:

(1) Diffusion-limited pair annihilation and coagulation are equivalent to each other on any lattice and for arbritrary hopping and annihilation rates. The time-dependent density and density correlations of the mixed process have a simple expression in terms of the same quantities of the pure annihilation process (see Eq. (26)).

(2) In one dimension with nearest neighbour hopping and infinite annihilation rate the m-point correlation function for an arbitrary N-particle initial state is given by correlation functions for a system with dual hopping rates (36) with at most $2m$ particles initially. These correlation functions can be expressed in terms of single-particle conditional probabilities (see (37), (40)), (41)). The derivation rests on a free fermion formulation of path integrals for annihilating random walks in one dimension. (3) Specifically for random initial conditions with density $1/2$ one gets both the exact and approximate results of Sec. 5 the particle density.

(4) For environments satisfying the assumptions detailed in Sec. 5 the density at site k at time t with a random initial state is equal to the return probability of a single particle in the dual environment at time $2t$ (see (47)).

Expressing the density in terms of the return probability has been done for

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computational convenience, not for physical reasons. Clearly, this relation is correct only in one dimension and only under the conditions outlined above. An open question which needs further investigation is the classification of hopping environments where these assumptions hold. It is also of interest to study universality of the density amplitude with respect to the initial density. This should be relatively straightforward in the approach developed above and is under investigation. A promising application of our results are disordered systems [3, 22] where further analysis requires taking a disorder average over products of single-particle conditional probabilities. Random walks in random environments are well-studied [11, 12] and, returning in our discussion to real systems such as exciton annihilation on polymers, one expects from this knowledge to gain considerable insight into the behaviour of diffusion-limited annihilation in one-dimensional disordered media.

Acknowledgments

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